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CARBON ADSORPTION STUDIES

OF

LIME TREATED PRIMARY EFFLUENT

RESEARCH BRANCH

MINISTRY OF THE ENVIRONMENT

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LIME TREATED PRIMARY EFFLUENT

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ABSTRACT

Pilot plant investigations were conducted to determine the effectiveness of granular activated carbon in removing organic material from the primary effluent of the Newmarket sewage treatment facility. The total system was: lime precipitation for phosphorus, coarse organics and suspended solids removal, followed by sand and activated carbon filtration for further solids and organics removal.

Following laboratory adsorption isotherm tests to determine the relative effectiveness of various activated carbons, the pilot column test with Filtrasorb 400 was carried out to define linear flow rates, backwash rates, column exhaustion times and other features.

INTRODUCTION

Carbon systems to treat municipal wastewater have proved to be very successful in the United States, in U.S.S.R. and many countries in Europe. Adsorption is one of the new processes for organic wastewater treatment since the introduction of activated sludge in the early 1900's. Activated carbon is perfectly suited for this application as municipal wastes may contain thousands of inorganic and organic chemicals, along with biological organisms. Activated carbon can remove almost all of these impurities and produce water that is suitable for many re-use applications.

Activated carbon, an amorphous form of carbon, is specially treated to achieve a very large surface area, ranging from 300 to 2,000 m^2/g. The large surface area indicates a very highly developed internal pore structure which enables the carbon to adsorb gases and vapours from gases and dissolved or dispersed substances from liquids.

Measurements of the distribution of pore sizes, using porosimeters have shown the existence of three types of pores in activated carbon; macropores of approximately 1 μm in diameter, transitional pores between 15 nm and 1 μm diameter, and micropores of less than 1 nm diameter. Transitional pores play a major role in adsorption of solutes from solution and micropores are essential for the effective adsorption of gases. Macropores have little adsorptive capacity, but facilitate diffusion within carbon particles. Two conflicting factors have to be taken into account during manufacture;

while adsorptive capacity increases as the porosity of the carbon is increased, the resistance to abrasion tends to decline, with the result that highly porous carbons have poor regenerative properties.

The mechanism of adsorption by carbon is an irreversible adsorption process. Limitation of the rate of uptake of solutes from solution by porous activated carbon depends on properties of the adsorbates, temperatures and available surface area. In natural waters and wastewaters, the adsorption process is also influenced by environmental variables and the nature of the solute system. Influencing factors include temperature, hydrogen ion concentrations, degree of turbulence, molecular structures and physico-chemical properties of the adsorbates and competing solute. For a particular adsorption case it is important to distinguish between rate of adsorption equilibria and capacity, because some variables can influence the kinetic system and not the equilibrium system, or can have a different influence on each. For instance, an increase in temperature may increase the rate of sorptive removal of solute from solution by activated carbon but decrease the capacity for adsorption. An increase in hydrogen ion concentration usually enhances both rate and capacity for adsorption, while the presence of competing solutes may affect each adversely (1).

The interaction of an adsorbate with an adsorbent surface may involve short-range forces such as hydrogen bonding, dipole-dipole interactions, or the long-range electrostatic forces characteristic of ionic atmospheres. Sometimes both types of forces are involved and these may be

changed by appropriate chemical treatment of surface. Charge-transfer interactions probably occur when activated carbon is used to remove residual chlorine from water supplies and they may account for the outstanding ability of activated carbon to adsorb coloured organic substances (2).

Some organics resist biological treatments but are removed by granular activated carbon (3). The kinetic mechanisms can be explained and kinetic data can be correlated mathematically. The diffusion co-efficient evaluated from the kinetic data is independent of the solution flow rate and adsorbent particle size but appears to be dependent upon bulk liquid phase concentration of the solute (4).

The influence of molecular structure and other factors on adsorbability are presented in Table 1 (5).

Studies in the field of metallurgy have also indicated good adsorption of many metallic compounds by activated carbon (Table 2, 3, 4, 5, & 6) (6). The following general mechanisms are probably involved.

First, carbons will physically adsorb on their internal surface molecular compounds such as acids, complex ions, high molecular weight polymers or other nonpolar species. Second, by a relatively small number of oxygen complexes and other functional groups fixed in the carbon surfaces, a limited ion exchange action can take place. Thus, the heavier and higher valance ions can displace H^+, Na^+, Ca^{++}, and other such ions to fix certain metals. Third, carbon can induce precipitation of a supersaturated solution by nucleation and can reduce the solubility of a metallic salt. Colloidal sus-

TABLE 1

INFLUENCE OF MOLECULAR STRUCTURE AND OTHER FACTORS ON AD-SORBABILITY

1. Aromatic compounds are generally more adsorbable than aliphatic compounds of similar molecular size.

2. Branched chains are usually more adsorbable than straight chains.

3. Substituent groups affect adsorbability:

Substituent Group	Nature of Influence
Hydroxyl	Generally reduces adsorbability; extent of decrease depends on structure of host molecule.
Amino	Effect similar to that of hydroxyl but somewhat greater. Many amino acids are not adsorbed to any appreciable extent.
Carbonyl	Effect varies according to host molecule; glyoxylic are more adsorbable than acetic but similar increase does not occur when introduced into higher fatty acids.
Double bonds	Variable effect.
Halogens	Variable effect.
Sulfonic	Usually decreases adsorbability.
Nitro	Often increases adsorbability.

4. An increasing solubility of the solute in the liquid carrier decreases its adsorbability.

5. Generally, strong ionized solutions are not as adsorbable as weakly ionized ones; i.e. undissociated molecules are in general preferentially adsorbed.

6. The amount of hydrolytic adsorption depends on the ability of the hydrolysis to form an adsorbable acid or base.

7. Unless the screening action of the carbon pores intervene, large molecules are more sorbable than small molecules of similar chemical nature. This is attributed to more solute carbon chemical bonds being formed, making desorption more difficult.

TABLE 2

METALS OF HIGH ADSORPTION POTENTIAL

Symbol	Element	Toxicity	AWWA Goal or Tentative Target	Potential for Removal by Carbon
Sb	Antimony	Probably high	None yet	Highly adsorbable in some solutions
As	Arsenic		50 ppb	Good in higher oxidation states
Bi	Bismuth	Slight	None	Very good
Cr^{+6}	Chromium	High	10 ppb	Good, easily reduced
Sn	Tin	Nontoxic	None	Proven very high

TABLE 3

METALS OF GOOD ADSORPTION POTENTIAL

Symbol	Element	Toxicity	AWWA Goal or Tentative Target	Potential for Removal by Carbon
Ag	Silver	Slight	50 ppb	Reduced on carbon surface
Hg	Mercury	Very High	5 ppb	CH_3H_gCl adsorbs easily Metal filtered out
Co	Cobalt	Slight	None	Radioactive Co^{60} very dangerous. Trace quantities readily adsorbed, possibly as complex ions
Zr	Zirconium	Low	None	Good at low pH

TABLE 4

ELEMENTS OF FAIR-TO-GOOD ADSORPTION POTENTIAL

Symbol	Element	Toxicity	AWWA Goal or Tentative Target	Potential for Removal by Carbon
Pb	Lead	High	50 ppb	Good
Ni	Nickel	Slight	None	Fair
Ti	Titanium	Nil	None	Good
V	Vanadium	Slight	None	Variable
Fe	Iron	Nil	None	Fe^{+++} good, Fe++ poor, but may oxidize

TABLE 5

ELEMENTS OF LOW OR UNKNOWN ADSORPTION POTENTIAL

Symbol	Element	Toxicity	AWWA Goal or Tentative Target	Potential for Removal by Carbon
Cu	Copper	Nil	200 ppb	Slight, possibly good if complexed
Cd	Cadmium	High	10 ppb	Slight
Zn	Zinc	Nil	1 ppm	Slight
Be	Beryllium	High	None	Unknown
Ba	Barium	High	1 ppm	Very low
Se	Selenium	High	10 ppb	Slight
Mo	Molybdenum	Slight	None	Slight at pH 6-8, good as complex ion
Mn	Manganese	Low		Not likely, except as MnO_4
W	Tungsten	Slight	None	Slight

TABLE 6

MISCELLANEOUS INORGANIC WATER CONTAMINANTS

SUBSTANCE	REMARKS
Phosphorus	
P, free element	Not likely to exist in reduced form in water.
PO_4^{3-} phosphate	Not adsorbed but carbon may induce precipitation of $Ca_3(PO_4)2$ or $FePO_4$.
Free halogens	
F_2 fluorine	Will not exist in water
Cl_2 chlorine	Adsorbed well and reduced
Br_2 bromine	Adsorbed strongly and reduced
I_2 iodine	Adsorbed very strongly, stable
Halides	
F^- fluoride	May adsorb under special conditions
Cl^-, Br^-, I^-	Not appreciably adsorbed

pensions also can be broken by upsetting the surface charge structure protecting the colloidal particles. Fourth, commercial activated carbons contain traces or reduced forms of iron and other metals which can enter into metathetical reactions with metallic ions lower in the electromotive series, causing the heavy metal to be deposited on the carbon surface.

Removal or inactivation of viruses from polluted water is necessary to prevent the spread of disease. Use of activated carbon to adsorb polio virus and infectious hepatitis virus was reported in 1950; earlier, carbon was used to adsorb the virus of foot and mouth disease. Studies of the adsorption of Escherichia coli, bacteriophage T on activated carbon showed that the virus was not inactivated. The adsorption process with virus is reversible, obeys Langmuir isotherm and can be described as reversible second-order kinetics. The virus is adsorbed mainly on the surface, its size probably excluding it from pores (7, 8). The site on activated carbon which adsorbs bacteriophage T4 is probably a carboxyl group or lactone. Adsorption on carbon can be completely blocked by esterifying these groups. It is proposed that amino groups on the virus adsorb carboxyl groups on the carbon by electrostatic attraction. As pH decreases from the optimum of 7, adsorption rate decreases, presumably resulting from an increase of negative charge on the virus particles and carbon surface, causing greater repulsive forces between the viruses and carbon particles. The collision frequency therefore, is reduced (9).

Many industrial applications use carbon to purify process water. Carbon removes chlorine from water used in brewing and soft drink preparation. Carpet mills re-use dye rinse water by first treating the water with carbon to remove

colour bodies. Some alcoholic beverages such as wine and
whiskey utilize carbon to remove objectionable tastes
before consumption. In California, brine solutions used
in the processing of olives have been regenerated by carbon
adsorption.

Increasingly, activated carbon is becoming the
accepted treatment step in treating wastewaters for safe
disposal in lakes, rivers and the sea. A pesticide manu-
facturer in Oregon removes chlorinated hydrocarbons, phenols,
cresols with carbon before the wastewaters are discharged, to
comply with the State water quality standards (phenol and
cresol 2 ppm max.). A petroleum refinery in California
treats 2,900 US gallons per minute of water with COD of
250 mg/l. The COD is reduced by 95% by a carbon system that
cost one million dollars to build and 9¢ per 1000 US gallons
to operate.

Most advanced physicochemical processes for waste-
water treatment have involved "tertiary" treatment for
wastes previously treated by "secondary" biological treatment.
Now suggested is the direct application of a physicochemical
process for treatment of primary wastes involving chemical
clarification, filtration and adsorption by activated carbon.
Several factors have led to the idea that a primary wastewater
might be more suitable for direct treatment with activated
carbon than after it had undergone biological treatment. These
included the apparent difficulty of removing final traces of
organic material from secondary effluent by the use of
activated carbon and the reports of leakage of some organic
fractions through the activated carbon columns. Leakage probably

consists of non-adsorbable cell fragments produced during biological treatment, plus small organic molecules hydrolyzed in the biological treatment stage (10, 11 and 12). Field tests of the direct physicochemical process indicated that chemical clarification followed by filtration can remove essentially all of the suspended solids from primary effluent; that activated carbon adsorption effectively removes remaining soluble organic fractions; and that chemical clarification also removes phosphate and the activated carbon treatment effectively reduces any nitrate present in the primary effluent.

PLAN OF STUDY

The purpose of this study was to determine the effectiveness of granular activated carbon in removing organic material from the primary effluent of the Newmarket sewage treatment facility.

The Newmarket sewage treatment plant is a 2.0 MIGD conventional activated sludge plant recently modified to include phosphorus removal. Approximately 200 ppm of hydrated lime is added to the raw sewage in a rapid mix tank. Phosphorus removal through the precipitation of calcium phosphate complexes, takes place in the primary clarifier. As a result of the lime addition the primary effluent has a pH averaging 9.5.

Following laboratory adsorption isotherm tests to determine the relative effectiveness of various activated carbons in treating the Newmarket primary effluent, a pilot activated carbon column study was conducted. Tests were performed to define linear flow rates, backwash rates, column exhaustion times and other features.

EXPERIMENTAL PROCEDURE

The effectiveness of a carbon in removing selected contaminants can be predicted using equilibrium adsorption isotherms developed from batch tests. The isotherm is a plot of the contaminant (TOC, TOD, etc.) versus the equilibrium remaining in solution. A linear representation using a log-log conforms to the Fruendlich equation which relates the amount of contaminant in the adsorbed phase to that in solution by the expression:

$$\frac{X}{m} = Kc^{\frac{1}{n}}$$ where:

X = amount of impurity adsorbed

m = weight of carbon

c = equilibrium concentration of impurity in solution

K, n constants

The Fruendlich isotherm is limited in certain cases. This occurs where concentrated and complex waste-waters contain a significant portion of organic impurities not amenable to adsorption, resulting in constant residual regardless of the carbon dosage.

To determine the feasibility of using activated carbon to remove organics from the primary effluent of the Newmarket wastewater treatment plant, a series of isotherm tests of different activated carbons were performed. The plot of isotherms for all the activated carbons tested showed almost similar results, with the granular activated carbon Filtrasorb 400 being only slightly superior. The isotherm on lime treated clarified sewage samples at the Newmarket STP indicated that, one pound of carbon Filtrasorb 400 removes

0.013 pounds of TOD to attain a treatment objective of 60% TOD remaining. (See Fig.1.). Therefore, the choice of carbon was mainly influenced by the cost of carbon and the economy of operation.

The pilot plant was located at the Newmarket WPCP (Fig.2.). The pilot plant design was predicated on providing a simple and reliable adsorption system that also would be capable of receiving and removing the suspended solids from the primary effluent. The total system was lime precipitation for phosphorus, coarse organics and suspended solids removal, followed by sand and activated carbon filtration for further solids and organics removal. The pilot column test was carried out with Filtrasorb 400 granular activated carbon. Filtrasorb 400 has a US standard series sieve size of 12 x 40, with a mean particle diameter of 1.0 mm. The total surface area is 1,050 sq m/g, and bulk density is 25 lb/cu ft.

Newmarket primary effluent was pretreated by passage first through a 3.2 foot high sand filter and then pumped downflow through three similar tranparent columns connected in series, each 6 feet long and 5 inches in diameter, containing a total depth of 11.1 feet of granular activated carbon (40 lb.). Each column was fitted with a pressure gauge and sample port. The columns were backwashed when a pressure drop of 5 psi was reached. It was expected that this pressure drop would not be exceeded within a 24 hours period.

Carbon dosage m (mg/l)	Conc. remaining C (mg/l)	Conc. reduction X (mg/l)	Reduction per unit of carbon $\frac{X}{m}$
0	100	–	–
200	95	5	25
420	90	10	24
1000	80	20	20
2500	65	35	14
3660	56	44	12

Concentration of TOD per unit carbon dose $\frac{X}{m}$

Concentration of TOD unadsorbed (mg/l)

Adsorption isotherm of primary effluent with Filtrasorb 400 (pH – 9.5 ; T – 20°C)
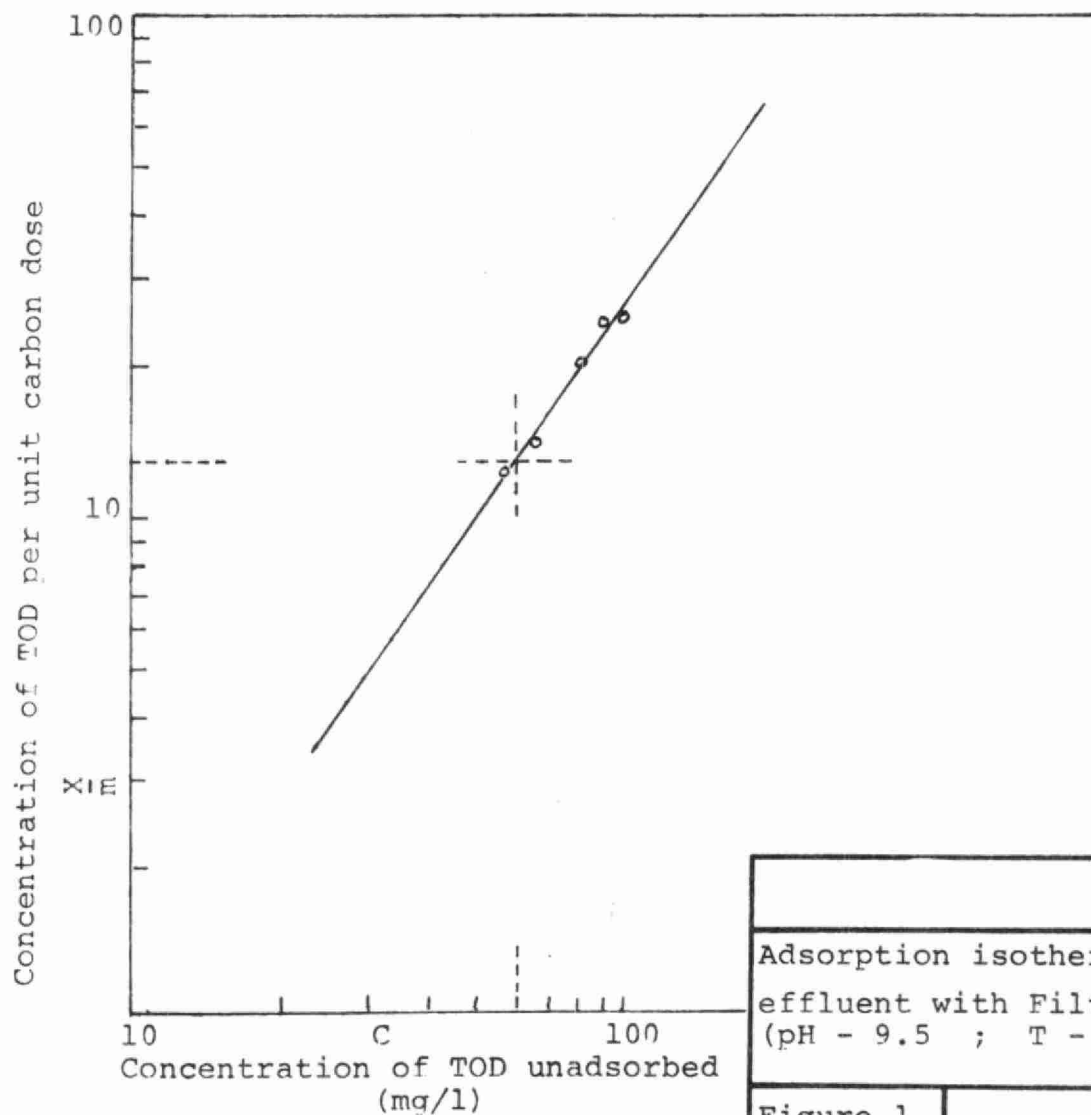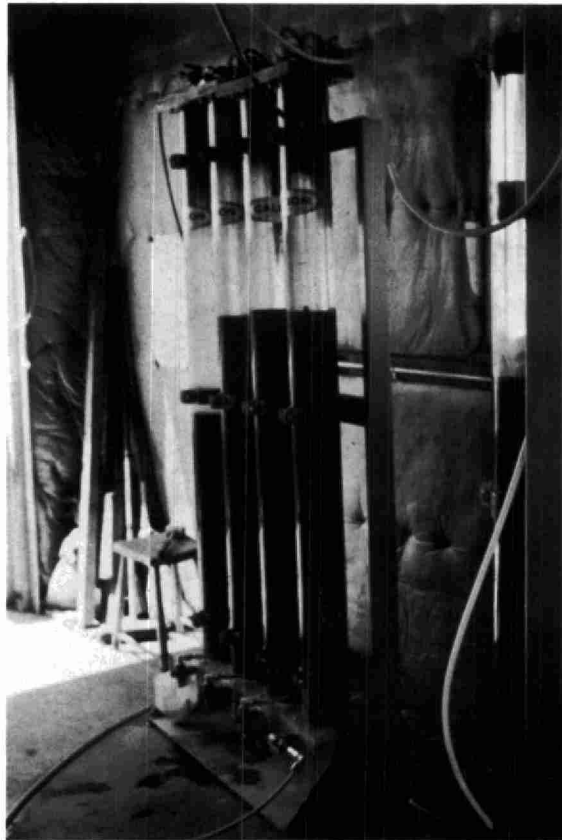
Figure 1

Pilot Plant at Newmarket
WPCP

Figure 2

RESULTS AND DISCUSSION

Breakthrough curves, based on composite samples
for TOD, TOC, BOD, COD at 4 gpm/sq ft. and the total depth
11.1 feet, in which the fractions of TOC, BOD, COD and TOD
percent remaining in the effluent were plotted as a function
of operating time, are shown in Figs. 3, 4, 5 and 6. Curves
for the intermediate bed depths and bed depth to service time
relationship are shown in Figs. 7, 8, 9 and 10. The constit-
uents contributing to the TOC, COD, BOD and TOD were not
completely removed and residuals ranging from 5 to 61 mg/l
and averaging 26 mg/l (TOC) remained in the effluent. In
order to establish whether an increase in retention time in
the carbon beds would effect more complete TOC removal, tests
were initiated at 2 gpm/sq ft. with the same apparatus. The
residual TOC was not decreased by a twofold increase in re-
tention time. No attempt was made to determine the chemical
nature of the constituents contributing to the residual TOC.
The only explanation that can be offered is that with the
high pH of the lime treated primary effluent (9.5 average)
the adsorption capacity of activated carbon is decreased and
that the residual is due to organic constituents that cannot
be adsorbed easily. However, as the objective of the study
was to determine the effect of several variables including
higher pH of effluent on the adsorption capacity of carbon no
attempt was made for pH adjustment before filtration.

During the test at 4 gpm/sq ft (0.5 gpm) a total of
approximately 50,000 gallons of primary effluent was passed
through the column assembly over an 86 day period. TOC break-
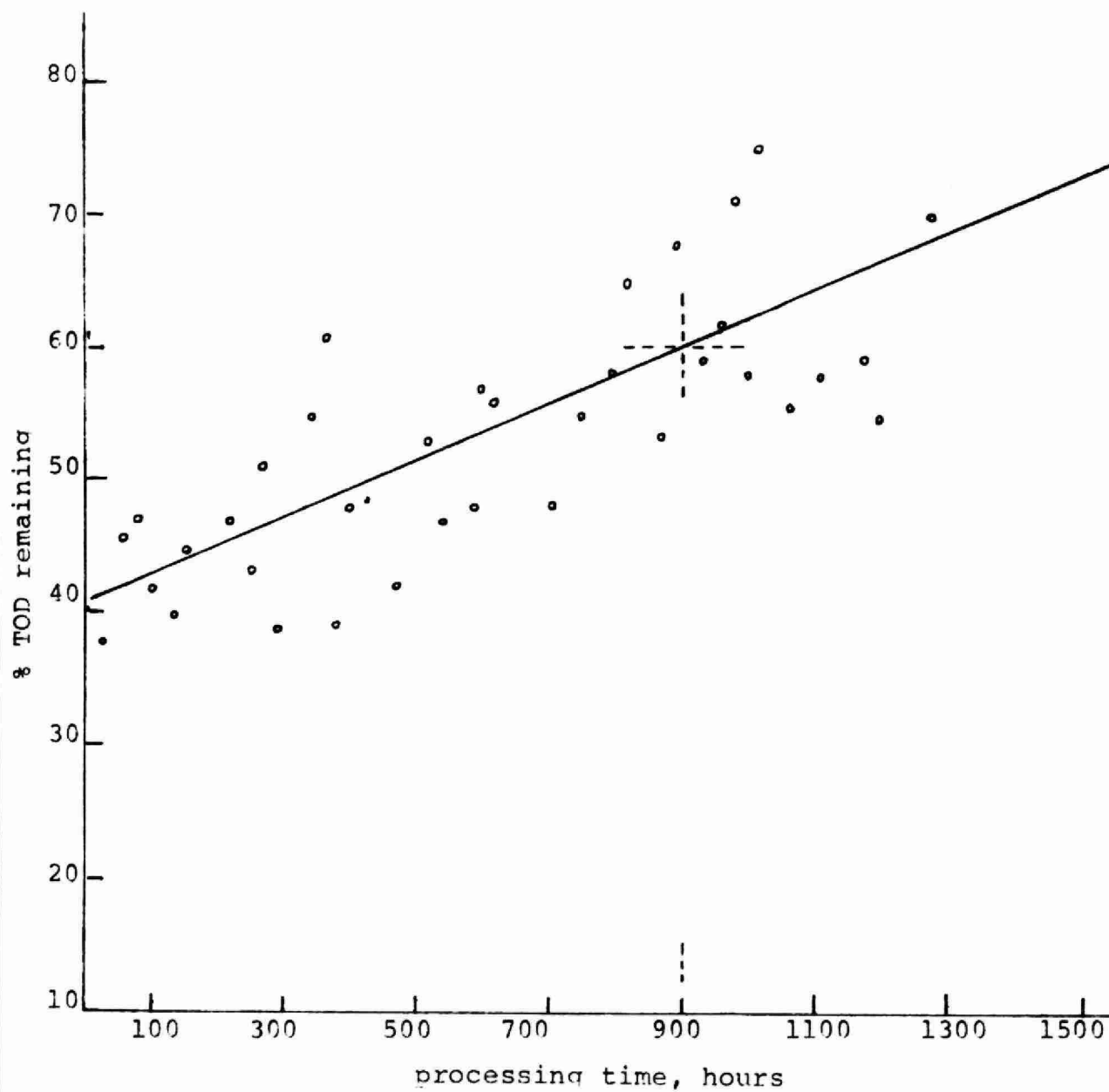points of 61% remaining were reached at 900 hours of operation

TOC breakthrough curve
Filtrasorb 400
Composite sample
Flow Rate: 4 gpm/ft^2
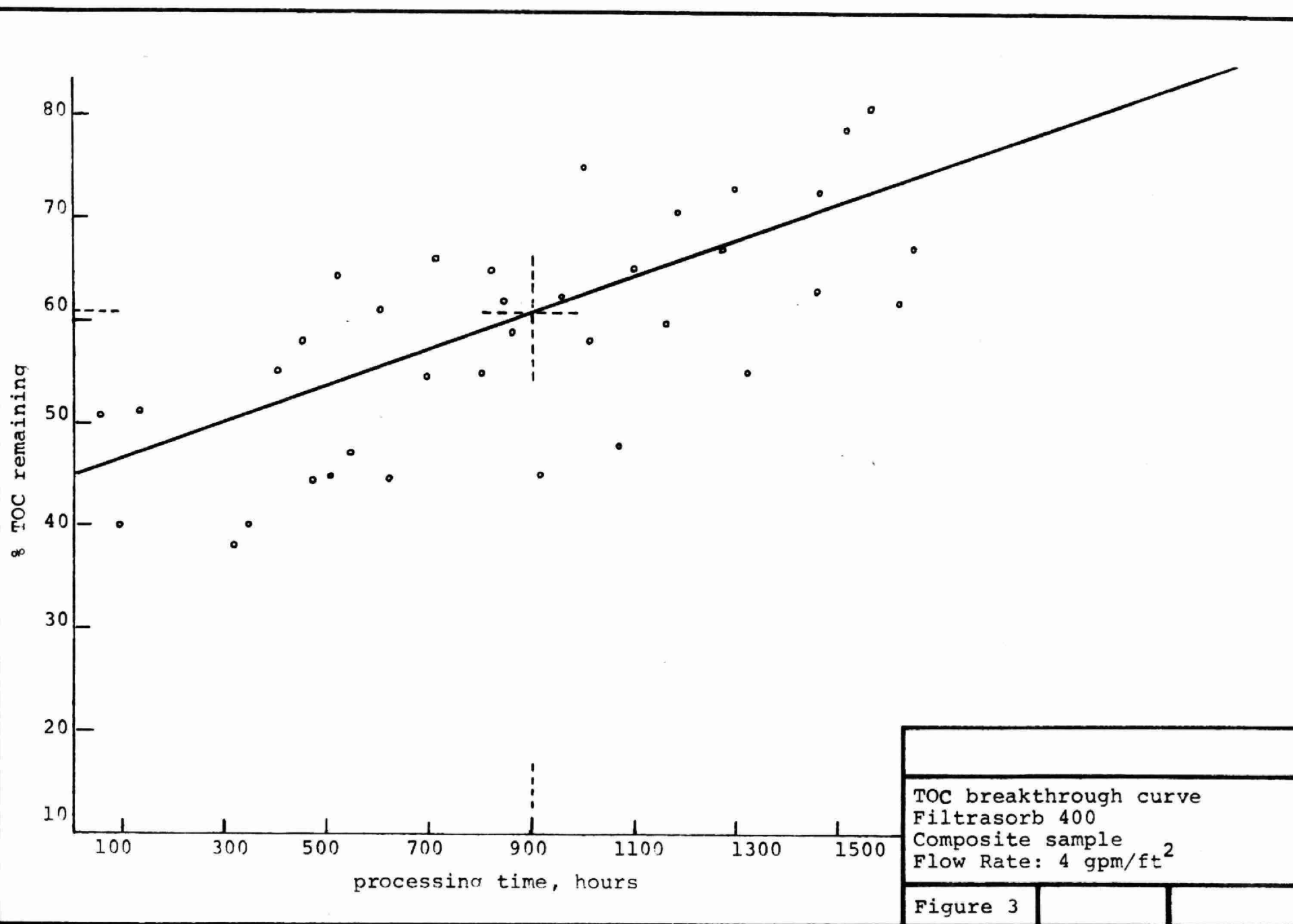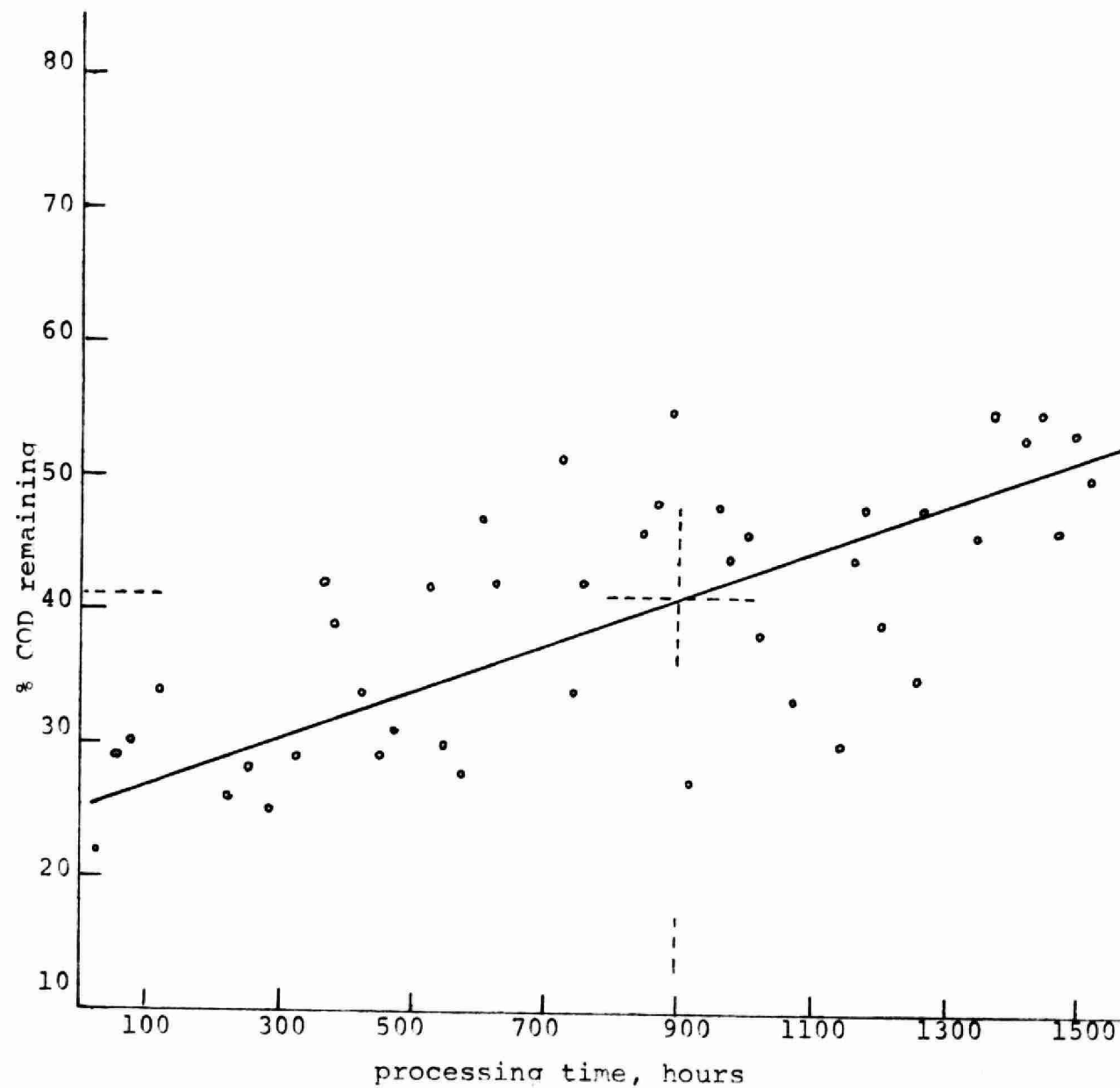
Figure 3

COD breakthrough curve
Filtrasorb 400
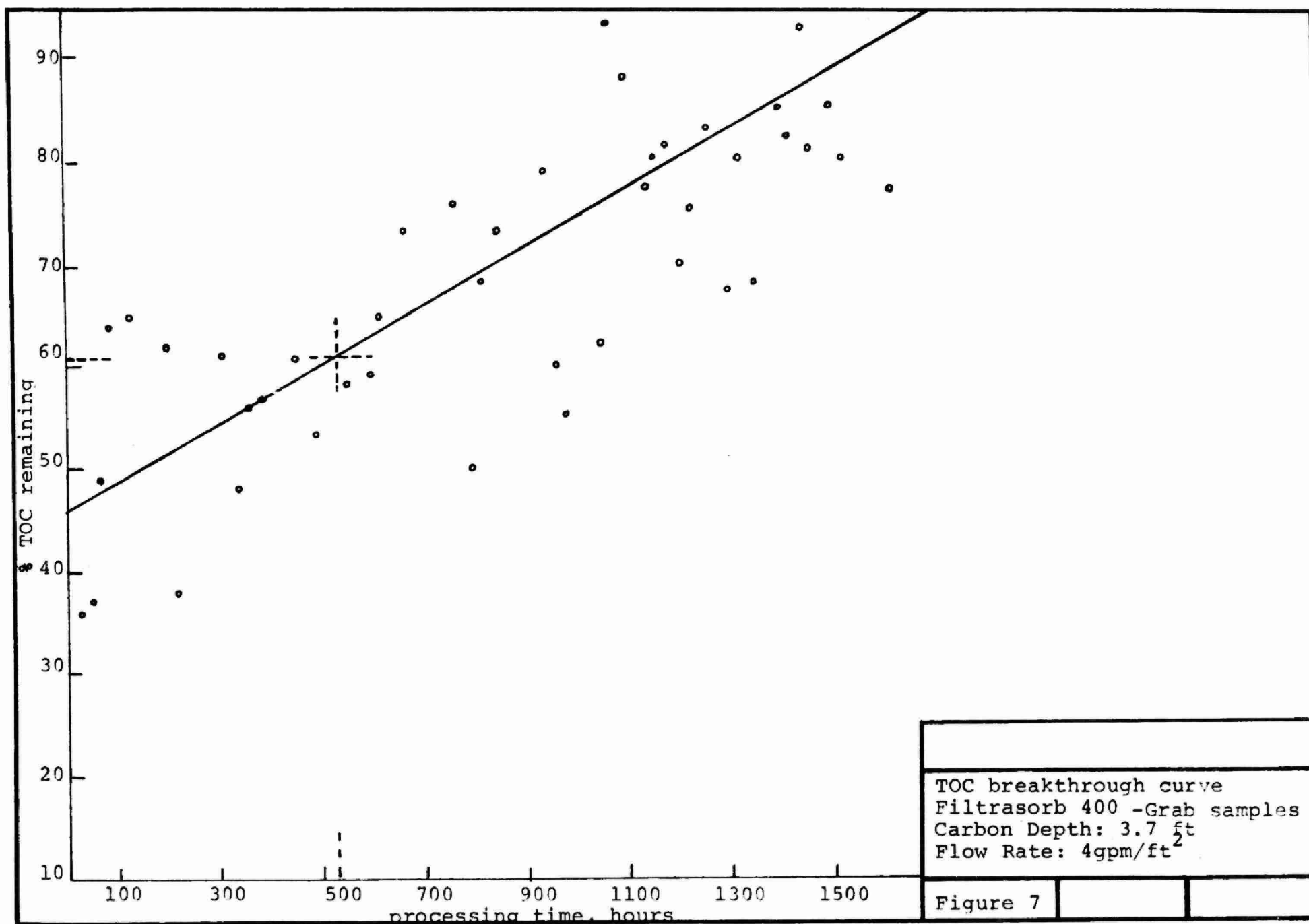Composite sample
Flow Rate: 4 gpm/ft^2
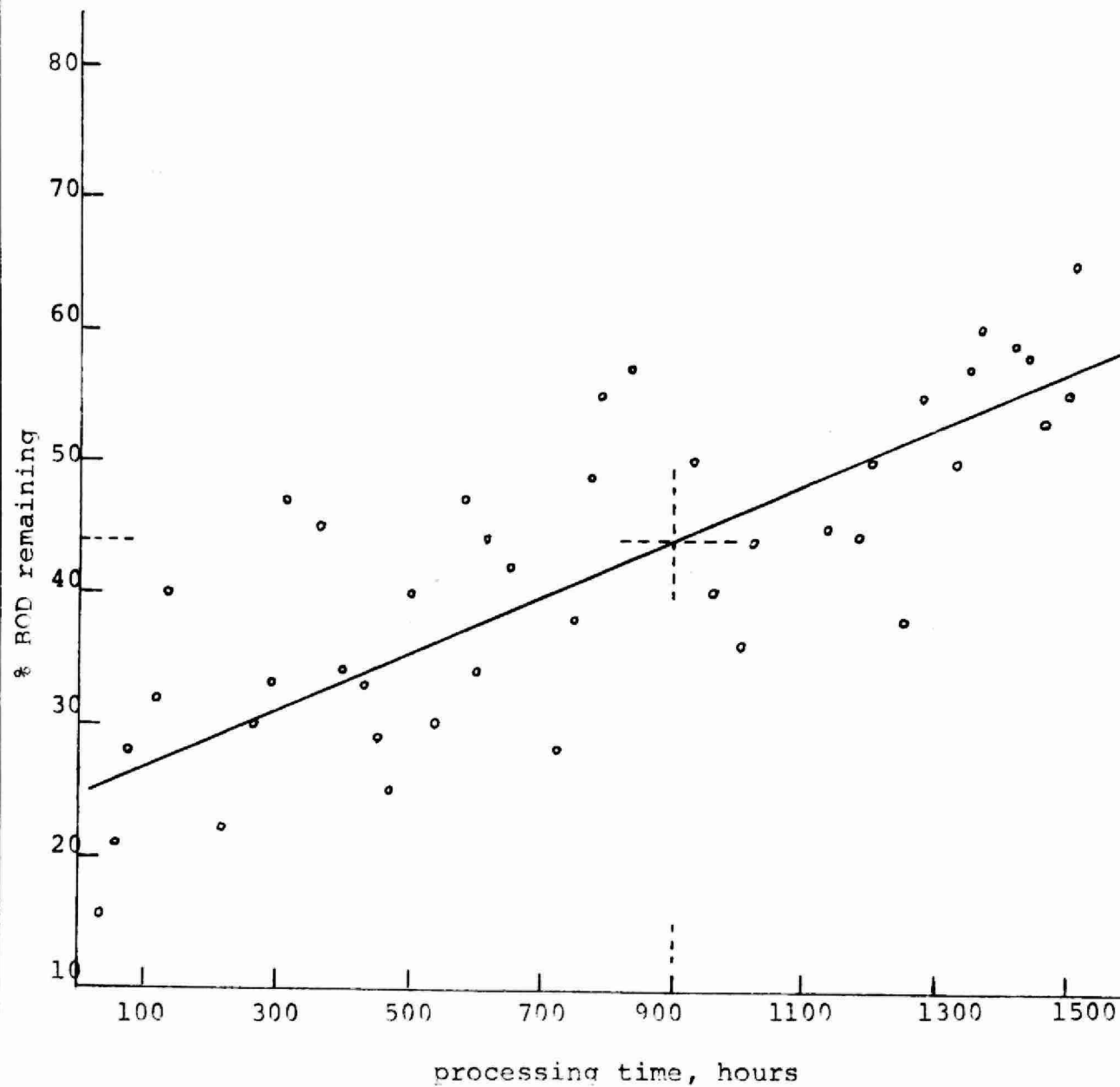
Figure 4

BOD breakthrough curve
Filtrasorb 400
Composite sample
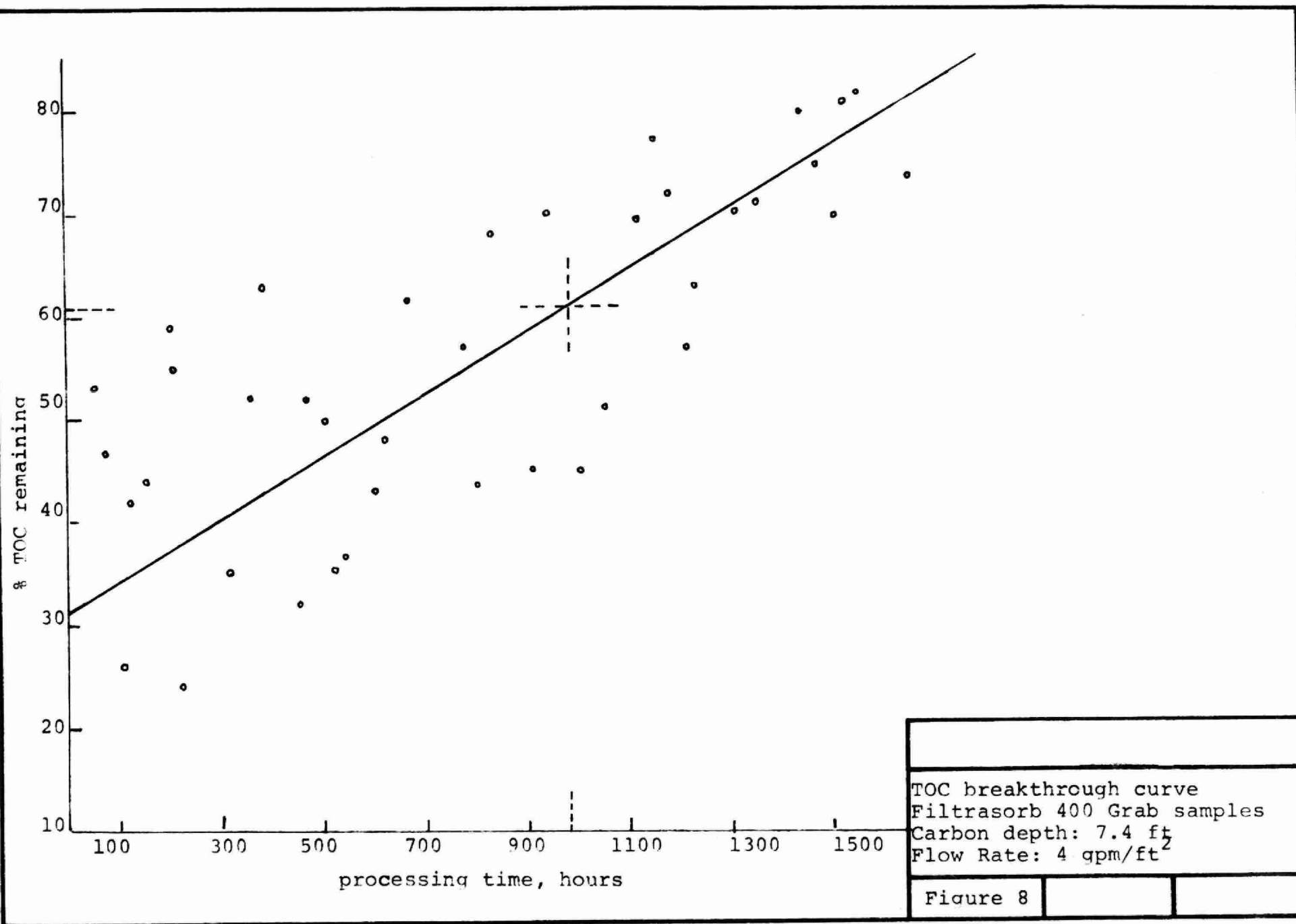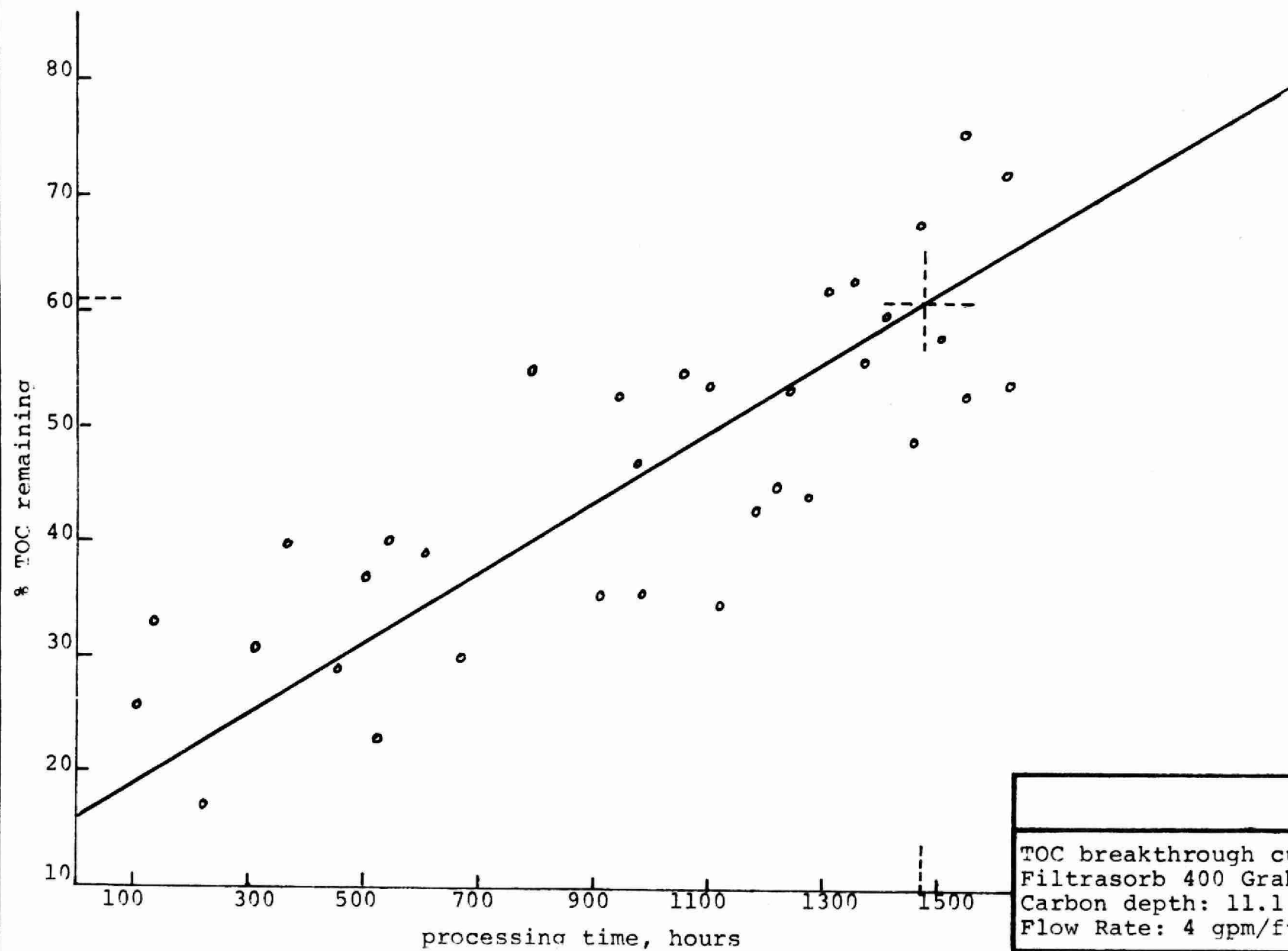Flow Rate: 4 gpm/ft^2

Figure 5

TOD breakthrough curve
Filtrasorb 400
Composite sample
Flow Rate: 4 gpm/ft^2

Figure 6

TOC breakthrough curve
Filtrasorb 400 -Grab samples
Carbon Depth: 3.7 ft
Flow Rate: 4gpm/ft^2

Figure 7

Figure 8 — TOC breakthrough curve. Filtrasorb 400 Grab samples. Carbon depth: 7.4 ft. Flow Rate: 4 gpm/ft^2

TOC breakthrough curve
Filtrasorb 400 Grab samples
Carbon depth: 11.1 ft
Flow Rate: 4 gpm/ft^2

Figure 9

Column No.	Bed Depth ft.	(61% TOC remaining) Service time: (hours)
2	3.7	530
3	7.4	980
4	11.1	1480

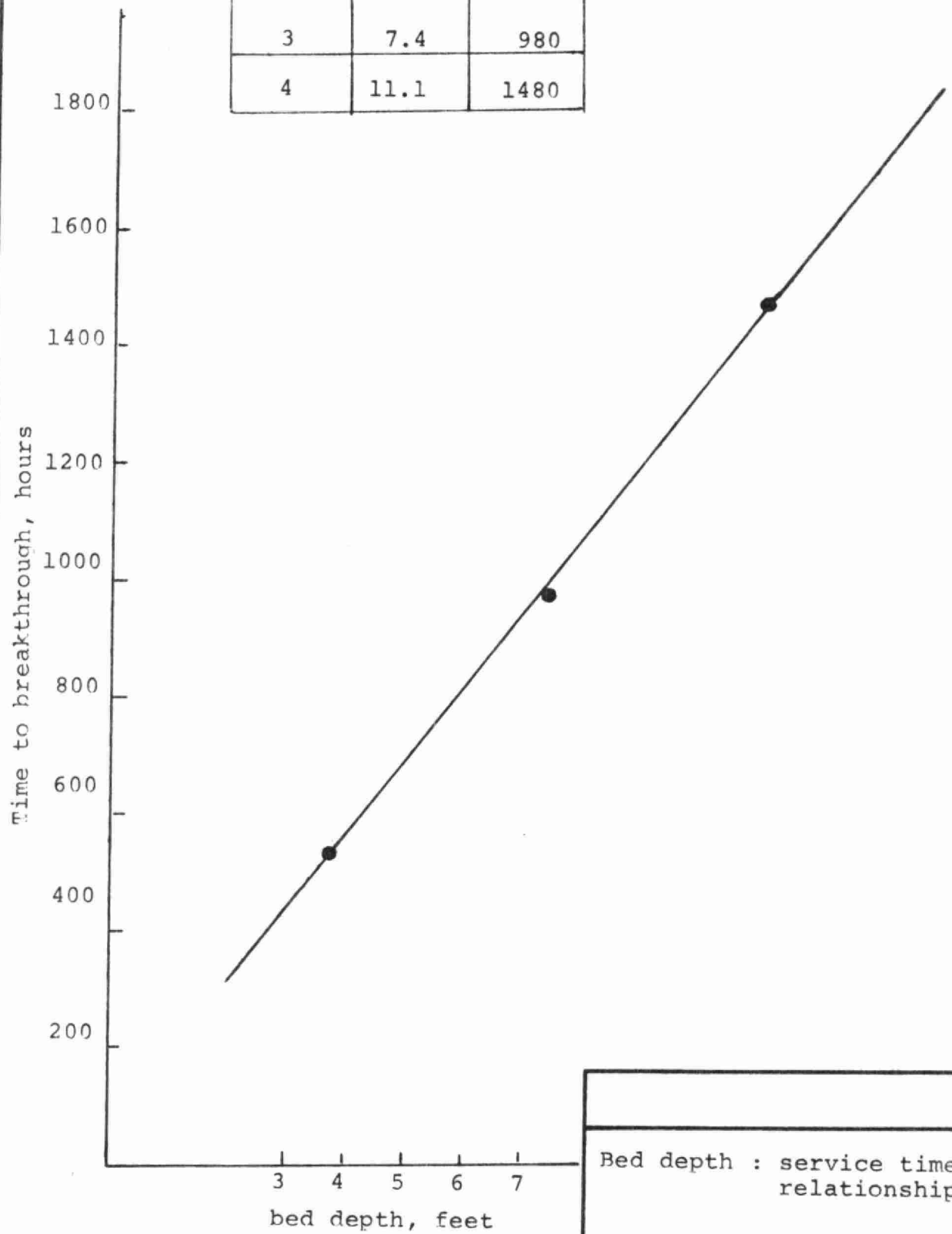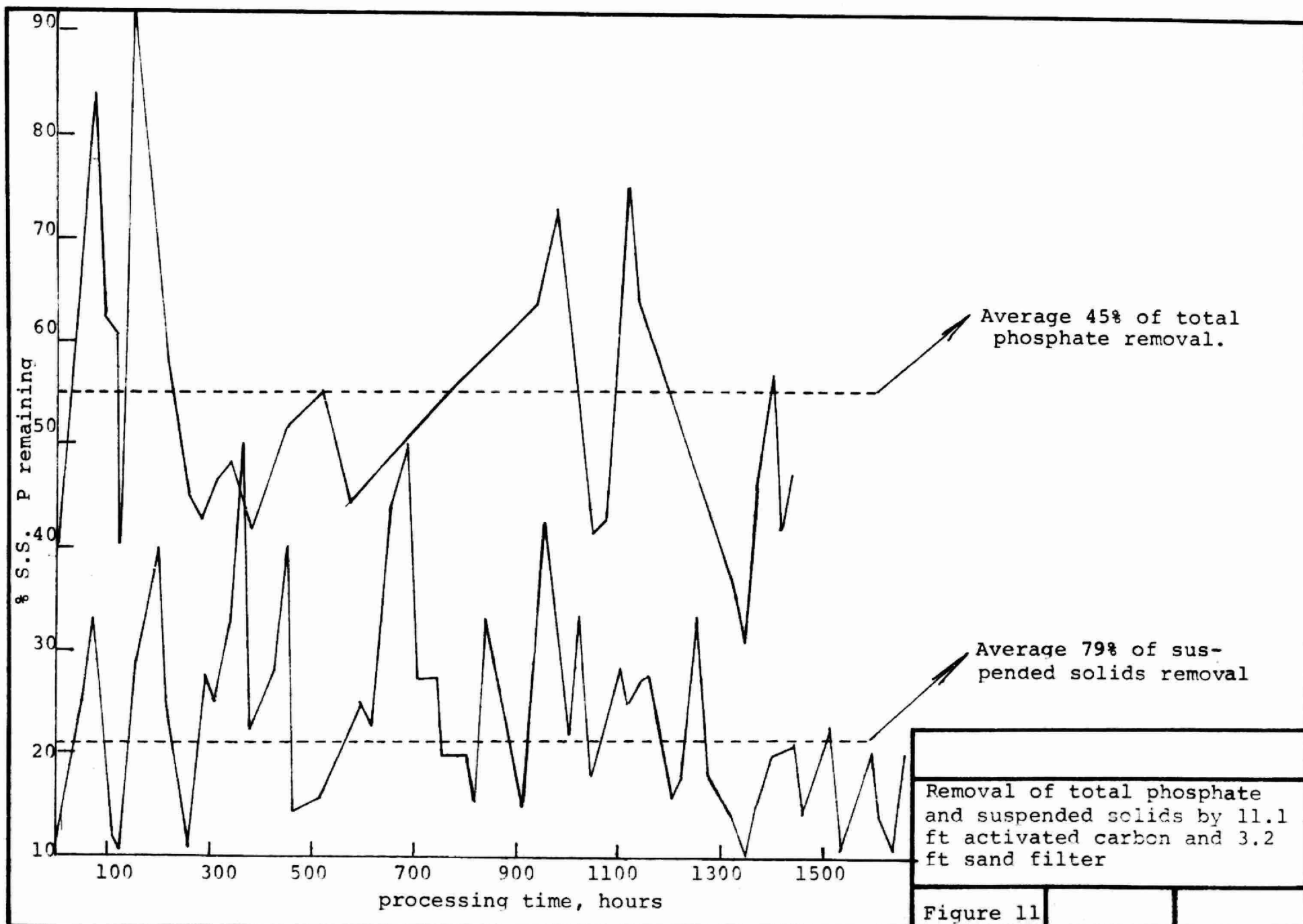Bed depth : service time relationship

Figure 10

when 27,360 gallons of primary effluent was passed through the column assembly.

The projected throughput indicates an exhaustion rate of 0.7 lb. of COD per lb. of carbon with 40% COD remaining, 0.307 lb. of BOD per lb. of carbon with 44% BOD remaining, 0.628 lb. TOD per lb. of carbon with 60% TOD remaining and 0.125 lb. of TOC per lb. of carbon with 61% TOC remaining.

Fairly good performance was obtained in relation to suspended solids and total phosphorus removals. An average reduction in suspended solids of 79% and in total phosphorus of 45% was achieved in the columns. The reduction in phosphorus is contributed to the "filtering" out of precipitated calcium phosphate complexes not settled out in the primary clarifier. (Figure 11).

CONCLUSIONS

The design of a system for the granular carbon treatment of the lime treated primary effluent at the Newmarket STP is complicated by the high pH and high suspended solids content of the primary effluent. The suspended solids content of the primary effluent averages about 100 ppm and unless reduced considerably by pretreatment, the suspended material will deposit on the carbon granules resulting in high pressure losses. Although the adsorption columns could be designed such that the accumulation of suspended matter could be periodically wasted from the bed, a more economical solution to the problem would probably be prefiltration.

Average 45% of total phosphate removal.

Average 79% of suspended solids removal

Removal of total phosphate and suspended solids by 11.1 ft activated carbon and 3.2 ft sand filter

Figure 11

The pH of the primary effluent averages around 9.5. Such a high pH has an adverse effect on the adsorption capabilities of activated carbon. To attain a treatment objective of less than 15 ppm BOD, the primary effluent pH would have to be adjusted to a pH of about 7 by a reclamation process or acid neutralization.

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